

FINAL REPORT

ASSERT Award:
Mapping Electrochemical Oxidation Pathways at Modified-Metal Catalysts

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Carol Korzeniewski

Texas Tech University
Department of Chemistry and Biochemistry
Lubbock, TX 79409-1061

Phone: 806/742-4181
Fax: 806/742-1289
Email: Carol.Korzeniewski@ttu.edu

ONR Program Officer: Richard Carlin

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14. ABSTRACT A small volume electrolysis technique that allows the quantitative determination of soluble by-products of electrochemical reactions on low surface area electrodes was developed during the project period. Chromatographic and wet-chemical assays were used to analyze for reaction by-products following brief electrolysis periods (5-10 min) of small (50-100 µL) sample volumes. The technique was applied to investigate effects of surface structure and composition on the oxidation pathways of small organic molecules at single crystal electrodes, bulk Pt-Ru alloys and supported fuel cell catalysts.					
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Project Description:

The main objective of the parent award (Probing Step Density Effects on Reactions at Single Crystal Electrodes, N00014-96-1-0448) is to probe elementary steps in the reaction of small organic molecules on electrode catalysts with the aim of understanding energy transfer processes relevant to fuel cells. Molecular adsorption and reactivity is investigated with the use of electrochemical and *in situ* spectroscopic techniques. The ASSERT award enabled the development of a small volume electrolysis technique that allows soluble by-products of electrochemical oxidation reactions to be determined quantitatively. Electrochemical reactions are carried out in a small volume of sample (50-100 μL). Following a brief electrolysis period (5-10 min) the solution is analyzed for reaction by-products with the use of chromatographic or wet-chemical assays. The approach was initially applied to investigate surface structural effects on ethanol oxidation pathways [1]. Ion chromatography was used to determine the acetate produced during the reaction of ethanol at Pt single crystal electrodes. Application of the small volume electrolysis technique was expanded to include the quantification of aldehyde and carboxylate compounds that formed as partial oxidation products following the reaction of alcohols on low surface area (0.1 cm^2), bead-type single crystal electrodes [1-3].

Subsequently, the technique has been employed to investigate the yields of formaldehyde formed during methanol electrochemical oxidation reactions [4,5]. Formaldehyde was determined with a fluorescence assay. Formaldehyde was observed in yields of up to 30 % following reaction periods of a few minutes on polycrystalline Pt and Pt-Ru electrodes at 0.5 V (vs. RHE) and ambient temperature. The approach was extended to study methanol oxidation pathways on bulk Pt and Pt-Ru alloy electrodes, and Vulcan carbon supported Pt and Pt-Ru fuel cell catalysts in Nafion.

The small volume electrolysis technique and approach to the study of methanol oxidation pathways are described in the attached papers.

References and Publications that Resulted Directly From Research Performed Under the ASSERT Award:

1. Tarnowski, D.J.; Korzeniewski, C. "Effects of surface step density on the electrochemical oxidation of ethanol to acetic acid" *J. Phys. Chem. B* **101** (1997) 253-258.
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Presentations of Research Performed Under the ASSERT Award:

Korzeniewski, C "Strategies for investigating the surface electrochemistry of simple molecules that serve as fuel cell reactants and intermediates" Texas A&M Univeristy, Commerce, Department of Chemistry, March 1999: Commerce, TX (invited).

Childers*, C.; Korzeniewski, C. "Formaldehyde yields from methanol electrochemical oxidation on solid platinum and supported catalysts" *Pittsburgh Conference*, March, 1999: Orlando, FL.

Korzeniewski, C. "Vibrational coupling as a probe of adsorption and reactivity at electrode surfaces" Purdue University, Department of Chemistry, March 1999: West Lafayette, IN (invited).

Korzeniewski, C. "Vibrational coupling as a probe of adsorption and reactivity at electrode surfaces" University of Illinois, Department of Chemistry, April 1999: Urbana, IL (invited).

Korzeniewski, C. "Fuel cell reactions probed by infrared spectroscopy at above ambient temperatures and wet chemical methods" ARO/DARPA sponsored Workshop on designed catalysts for fuel processor/fuel cell systems, April 1999: Chicago, IL (poster, invited).

Korzeniewski, C.; Childers, C.; Huang, H. "Conditions Under Which Formaldehyde Can Accumulate During Methanol Electrochemical Oxidation on Solid Platinum and Nanostructured Catalysts" *195th Meeting of the Electrochemical Society*, May, 1999: Seattle, WA.

Korzeniewski, C.; "Investigating the surface electrochemistry of simple molecules that serve as fuel cell reactants and intermediates" *DOE-ONR sponsored workshop on Basic and Applied Research for Proton-Exchange Membrane Fuel Cells*, October 6-8, 1999: Baltimore, MD (invited).

Korzeniewski, C "Strategies for investigating the surface electrochemistry of simple molecules that serve as fuel cell reactants and intermediates" Creighton Univeristy, Department of Chemistry, March 1999: Omaha, NE (seminar for graduate recruiting).

Korzeniewski, C. "Vibrational coupling as a probe of molecular adsorption at different structural sites on surfaces", *Engineering Foundation Conference on Surface Characterization of Adsorption & Interfacial Reactions II*, Jan. 1998: Kona, HI (invited).

Korzeniewski, C. "Probing step density effects on reactions at single crystal electrodes" AFSOR/ONR Electrochemistry Science & Technology Program Review, Jan. 1998: Ventura, CA.

Korzeniewski, C. "Surface structural effects on organic oxidation pathways probed by electrochemical, spectroscopic and chromatographic techniques", *Gordon Research Conference on Electrochemistry*, Jan. 1998: Ventura, CA (invited).

Korzeniewski*, C.; Kim, C.S.; Tarnowski, D. J., Dailey, A. "Effects of surface nanoscale terraces on molecular adsorption and reactivity", *215th ACS National Meeting*, March-April 1998: Dallas, TX. (Keynote speaker in Symposium on Electrochemistry and Nanostructured Materials)

Korzeniewski, C "Investigating the surface electrochemistry of simple organic molecules that serve as fuel cell reactants and intermediates" Northern Arizona University, Department of Chemistry, April 1998: Flagstaff, AZ (seminar for graduate recruiting).

Kardash*, D.; Childers, C.; Korzeniewski, C. "Adsorption and oxidation of small molecules on electrodes probed by IR spectroscopy and wet-chemical methods" *Federation of Analytical Chemistry and Applied Spectroscopy Societies*, Oct., 1998; Austin, TX. (student poster)

Korzeniewski, C "Strategies for investigating the surface electrochemistry of simple molecules that serve as fuel cell reactants and intermediates" University of New Mexico, Department of Chemistry, Nov. 1998: Albuquerque, NM (invited).

Korzeniewski, C. "Vibrational coupling as a probe of adsorption and reactivity at surfaces with ordered step and terrace structures", Pacific Northwest National Laboratory, Jan. 1997: Richland, WA (invited).

Korzeniewski, C. "Vibrational coupling as a probe of adsorption and reactivity at surfaces with ordered step and terrace structures", University of Washington, Department of Chemistry and Chemical Engineering, Jan. 1997: Seattle, WA (invited).

Korzeniewski, C. "Vibrational coupling as a probe of adsorption and reactivity at surfaces with ordered step and terrace structures", Department of Chemistry, University of Utah, Feb. 1997: Salt Lake City, UT (invited).

† C. Korzeniewski, "Probing step density effects on reactions at single crystal electrodes" Office of Naval Research Program Review, April 2-4, 1997: Atlanta, GA.

Korzeniewski*, C.; Tarnowski, D.J.; Kim, C.; Dailey, A. "Step density effects on adsorption at platinum single crystal electrodes", *191st Electrochemical Society Meeting*, May, 1997: Montreal, Quebec, Canada. (invited)

Korzeniewski*, C. Dailey, L.A.; Huang, J. "Surface structural effects on adsorption and reactivity at platinum single crystal electrodes" *Surface Electrochemistry*, Sept. 7-10, 1997: Alicante, Spain (invited).

Korzeniewski*, C.; Tarnowski, D.J.; Dailey, A. "Ion chromatography in the study of electrochemical reactions on single crystal electrodes: Mapping pathways of fuel cell reactants", *International Ion Chromatography Symposium 1997*, Sept. 1997: Santa Clara, CA (invited).

Korzeniewski*, C, "Analytical Studies of Metal-Liquid Interfaces", San Jose State University, Sept. 1997: San Jose, CA (departmental seminar for graduate recruiting).

Formal Technical Reports Filed: none

Patents (indicate status, e.g., filed, issued): none

Number of Students Supported on ASSERT Award During the Funding Period (minimum of 1/4 of their support):

Post Doctoral: 0 Doctoral: 1 Q: Masters: 1 Undergraduate: 1

Of these students, the number who were:

Females: 2

Under-represented Ethnic groups: 0

Students Supported:

Christina Childers (M.S. Texas Tech University, 1999)
Dawn Kardash (Ph.D. Texas Tech University, 2000)
Austin Dailey (B.S., Texas Tech University, 1998)

LETTERS

Formaldehyde Yields from Methanol Electrochemical Oxidation on Platinum

Carol Korzeniewski* and Christina L. Childers

Department of Chemistry & Biochemistry, Texas Tech University, Lubbock, Texas 79409-1061

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Formaldehyde formed in the electrochemical oxidation of methanol was measured in order to assess its importance as a reaction intermediate and potential source of efficiency loss in direct methanol fuel cells. Formaldehyde generated from 15 mM methanol in 0.1 M HClO₄ at fixed potentials with a small volume electrolysis arrangement was determined with a sensitive fluorescence assay. The formaldehyde yields approached 30% of the total electrolysis charge at 0.2–0.3 V (vs Ag/AgCl). The percentages dropped at more positive potentials, as other oxidation pathways became dominant. However, formaldehyde production continued to increase with potential, maximizing near 0.5 V. This study demonstrates that formaldehyde, which is often not detectable with modern in situ analysis techniques, can be produced during methanol electrochemical oxidation in significant amounts. A fluorescence assay specific for formaldehyde is suggested for use in parallel with in situ measurements.

Introduction

Interest in the development of direct methanol fuel cells has motivated many studies of methanol electrochemistry.^{1–6} Methanol dissociative chemisorption occurs readily on clean platinum, but sustained reaction is impeded by partial oxidation products that poison the surface. Furthermore, the complete oxidation of methanol to CO₂ requires potentials that have been unacceptably high for energy production. Mixed metal catalysts, particularly Pt–Ru, improve the conversion efficiency, in part through an enhancement in the kinetics of the water activation step ($\text{H}_2\text{O} \rightarrow \text{OH}_{\text{ads}} + \text{H}^+ + \text{e}^-$).⁶ Even with these advances, further gains in catalyst performance are desired.

In mechanistic studies of methanol electrochemical oxidation, attention has tended to focus on partially oxidized adsorbed species.¹ Adsorbed CO has been identified as a key surface poison and reaction intermediate.^{1–9} There is evidence that adsorbed –CHO and –COH also form, but these species are difficult to detect on electrodes.^{1–4,9,10} Methanol oxidation pathways to CO₂ via these non-CO intermediates and formate-

like species are believed to parallel the route through adsorbed CO.^{1–4,a,c,7b,9,10} There has been recent interest in the later pathways,^{2,4} since at low potentials their optimization can lead to improvements in energy conversion efficiency.

Methanol electrochemical oxidation can also proceed through soluble intermediates, although these species have received less attention than adsorbates.¹ Early studies established that formaldehyde and formic acid form in solution during reaction (ref 11a,b and references therein). Methyl formate (HCOOCH₃) and 1,1-dimethoxymethane (H₂C(OCH₃)₂) have also been detected and decrease with increasing water:methanol ratios.^{11a,b,d,13–16} Of the soluble intermediates mentioned, formaldehyde is especially difficult to track. The modern in situ analysis techniques, mass spectrometry and infrared spectroscopy, suffer interferences from other species in solution. Mass spectrometry is hampered by the coincidence of formaldehyde and methanol mass fragments.^{15,16} Infrared spectroscopy is limited by the aqueous solution chemistry of formaldehyde, which forms the gem-diol (H₂C(OH)₂)^{17–19} and therefore overlaps with water vibrational bands.^{13,20–22} Detailed reports of formaldehyde

* Corresponding author. Email: bfor@ttacs.ttu.edu.

yields from methanol electrochemical oxidation have relied on separate colorimetric^{11a,b,d} or liquid chromatographic assays.^{11c,e}

With reliance on the in situ techniques mentioned above for molecular level studies of methanol electrochemical oxidation in recent years, we wondered whether formaldehyde, if it is produced in these reactions, has gone undetected. Formaldehyde was observed in early studies of methanol oxidation¹¹ but has been largely ignored with the focus on adsorbed intermediates. As a species formed in the early stages of reaction, the accumulation of formaldehyde in solution can lower the energy conversion efficiency. Therefore, we performed analytical measurements to track formaldehyde formed from methanol electrochemical oxidation with high specificity.

In the present study, methanol samples were analyzed for formaldehyde with a sensitive fluorescence assay^{23,24} following short (6 min) electrolysis periods with a small volume electrochemical cell. Formaldehyde was detected at levels substantially above background between 0.2 and 0.6 V (vs Ag/AgCl) and accounted for a significant fraction of the total electrolysis charge between 0.2 and 0.4 V. This knowledge is important for interpretations of methanol electrochemistry and can help guide the design of catalysts and theories of methanol oxidation pathways.

Experimental Section

Reagents. All solutions were prepared with 18 M Ω water from a four-cartridge Nanopure system (Barnstead, Des Moines, IA). Perchloric acid (Aldrich, Milwaukee, WI) was obtained in 99.999% purity and used as received. Methanol (Burdick & Jackson, GC grade) was washed over alumina, filtered, distilled, and stored refrigerated. Glacial acetic acid, ammonium acetate, formaldehyde, and 2,4-pentanedione were obtained from Aldrich as reagent grade or better and used as received. Argon (Trinity Gases, Dallas, TX) was of ultrahigh purity.

Electrochemistry. A KCl saturated silver–silver chloride (Ag/AgCl) reference electrode was employed in all voltammetric experiments. The working electrode was a circular disk of polycrystalline Pt (4 mm diameter) mounted in a Teflon sheath. The Pt electrode was periodically polished mechanically with alumina down to 0.05 μ m followed by sonication to remove debris. Before each experiment the electrode was electropolished by repeated cycling in 0.1 M HClO₄ between about -0.4 and 1.8 V. Surface cleanliness was checked by observing sharp features in the hydrogen adsorption and oxide regions of a cyclic voltammogram recorded at 50–100 mV/s between -0.25 and 1.35 V (Figure 1A). When not in use, the electrode was stored in a ~35% HClO₄ solution.

Electrochemical cell potentials were maintained with a three-electrode potentiostat (PAR Model 273/86, Princeton, NJ) controlled through an IEEE-488 interface bus by a microcomputer running Model 270/250 Research Electrochemistry Software (PAR), version 4.00. The working electrode was electropolished in a conventional, glass three-electrode cell with a platinum counter electrode and a Ag/AgCl reference isolated behind a wetted, ground glass stopcock. Electrolysis experiments were conducted with the experimental arrangement shown in Figure 2.^{25,26} The platform was machined from a segment (~2 cm) of 1 in. diameter Kel-F rod. The sample was held in a shallow depression milled into one face of the rod. Narrow channels joined the sample solution to the reference and counter electrode compartments. These compartments connected to the platform through ~0.022 in. i.d. Teflon tubing. A Pt wire counter electrode was sealed with epoxy into a glass tube, which held 0.1 M HClO₄ and was capped to prevent leakage of solution

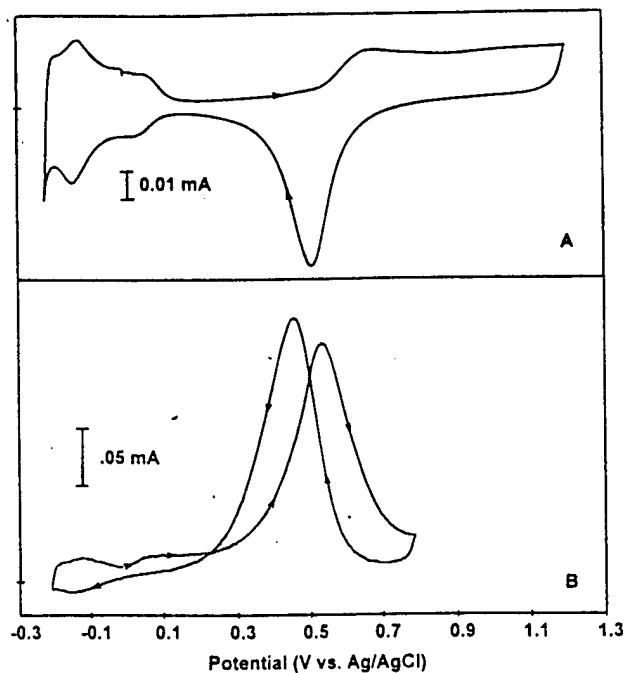


Figure 1. Cyclic voltammograms of polycrystalline Pt in 0.1 M HClO₄ (A) and 15 mM methanol in 0.1 M HClO₄ (B) recorded with the arrangement in Figure 2. Sweep rates were 100 mV/s.

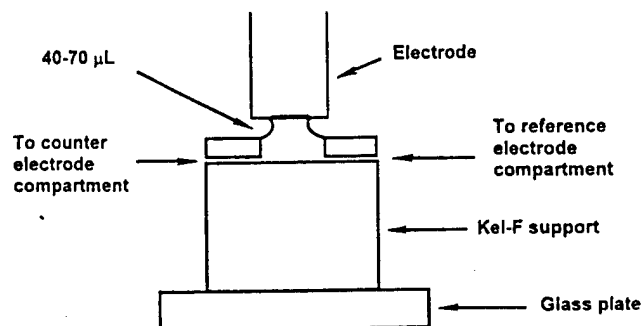


Figure 2. Arrangement for electrolysis and cyclic voltammetry experiments. Electrochemistry was performed with the assembly enclosed in an Ar-purged container. See text for details.

onto the sample platform. The reference electrode was isolated behind a wetted stopcock.

For methanol electrolysis experiments, 50 μ L of argon-purged 0.1 M HClO₄ was placed on the platform with a pipet. The electropolished Pt disk electrode, carrying ~5 μ L of electrolyte, was brought into contact with the solution on the platform and a cyclic voltammogram was recorded. The assembly was then lowered into a glass container and placed under Ar purge. The working electrode was raised, and 5 μ L of 0.18 M methanol in 0.1 M HClO₄ was added to and mixed with the 0.1 M HClO₄ solution on the platform. After an equilibration period of 20 s, the electrode was brought into contact with the sample solution with a potential of 0.0 V applied. The purge gas was then turned off to maintain quiescence, and the electrode was stepped to the electrolysis potential where it was held for 360 s. The electrolysis current was recorded, and the data were electronically stored for future use. At the end of the reaction period, the cell was removed from potential control and 50 μ L of sample was withdrawn from the platform and assayed for formaldehyde.

Formaldehyde Determination. Formaldehyde was determined fluorometrically as the 3,5-diacetyl-1,4-dihydrolutidine species^{23,24} by adapting the method of Dasgupta and co-workers.²³ The sample was added to 50 μ L of a solution that contained 2.0 M ammonium acetate, 0.05 M acetic acid, and

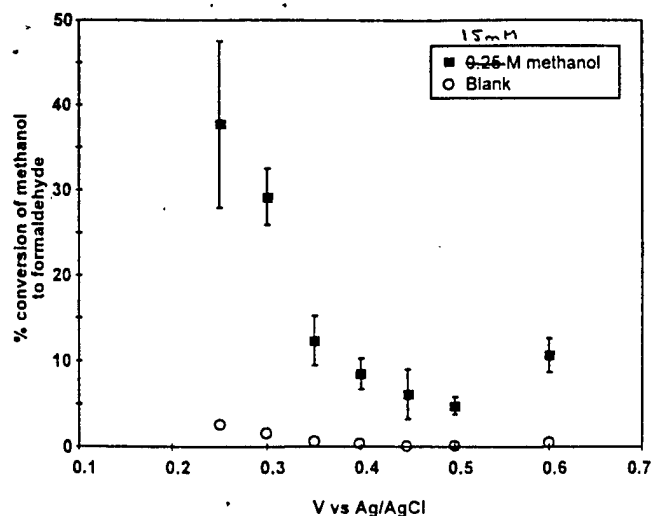


Figure 3. Plot showing the formaldehyde conversion efficiencies as a function of the electrolysis potential. Closed squares: the formaldehyde quantity following 360 s electrolysis of 15 mM methanol in 0.1 M HClO₄ ratioed to the corresponding electrolysis charge, multiplied by 100%. Open circles: the formaldehyde quantity following 360 s electrolysis of 0.1 M HClO₄ ratioed to the average methanol electrolysis charge at the corresponding potential, multiplied by 100%. Error bars represent the 95.5% confidence limit determined from ± 2 times the sample standard deviation.

0.02 M acetyl acetone and incubated at 60 °C for 5 min. Fluorescence was measured with an SLM 4800C Spectrofluorometer (SLM Instruments, Urbana, IL). Analytical determinations were performed with the excitation and emission wavelengths at 410 and 515 nm, respectively, with a 2 nm bandpass. Formaldehyde calibration curves were recorded with freshly prepared standards in the range 1.8×10^{-4} to 1×10^{-6} M.

Results and Discussion

Figure 1 shows cyclic voltammograms recorded with the arrangement displayed in Figure 2. The voltammogram of the platinum electrode in blank 0.1 M HClO₄ demonstrates the cleanliness of the system and the response of the electrochemical cell arrangement. In the methanol voltammogram, the basic features, such as the current maximum at 0.6 V and the anodic wave on the negative-going sweep, are consistent with previously reported voltammograms for methanol on platinum^{4c,7a,8a}.

Figure 3 reports the formaldehyde yields as a function of potential. The percent conversion is computed from the ratio of the charge required to produce the quantity of formaldehyde detected fluorometrically to the total charge passed during electrolysis. The formaldehyde yields are near 30% at the lowest potentials. The large error bars on the data obtained at 0.25 V arise from uncertainty in the electrolysis charge, likely from slow methanol turnover caused by extensive surface poisoning. In all cases, however, the formaldehyde produced was well above the background (see below). The drop in formaldehyde production to below 10% between 0.3 and 0.4 V coincides with a rapid increase in the cyclic voltammetric current, indicating that other reaction pathways become more dominant across this potential range. Several studies of methanol electrochemical oxidation on platinum report an increase in CO₂ production at 0.3–0.4 V (vs Ag/AgCl), which persists out to more positive potentials.^{2,4a,c,8a–d} It appears that water activation becomes facile at potentials greater than 0.3 V and promotes CO₂ formation, particularly from the oxidation of adsorbed CO and other adsorbed species.^{1,5a,8} This trend is

TABLE 1: Summary of Methanol Oxidation Current and Product Yields^a

potential (V vs Ag/AgCl)	average charge (mC)	average H ₂ CO quantity (pmol)	H ₂ CO yield (%) ^b	CO ₂ yield (%) ^c
0.2	0.09	122	26	5
0.25	0.11	226	38 ± 10	
0.3	0.40	565	29 ± 3	50
0.35	2.36	1720	12 ± 3	
0.4	2.62	1153	8 ± 2	80
0.45	6.48	1940	6 ± 3	
0.5	13.25	3299	5 ± 1	98
0.6	2.36	1310	11 ± 2	

^a Except for the CO₂ yields, all data were obtained from the 360 s electrolysis of 15 mM methanol in 0.1 M HClO₄ on polycrystalline platinum. ^b Error bars represent the 95.5% confidence limit determined from two times the sample standard deviation. The yield is computed from the charge required for H₂CO production ratioed to the total current passed. An H₂CO yield was computed for each experiment, and these values were averaged to give the percentages and uncertainties shown. The number of experiments performed at each potential was 3 (0.25 V), 5 (0.3 V), 3 (0.35 V), 7 (0.4 V), 3 (0.45 V), 12 (0.5 V), and 3 (0.6 V). ^c Data are from ref 2 for reactions of 0.1 M methanol in 0.1 M HClO₄ on Pt(100).

illustrated in Table 1, which compares the quantities of formaldehyde detected following reaction of methanol on polycrystalline platinum electrodes to the CO₂ yields determined in a recent study with Pt(100). The decline in the formaldehyde quantity relative to the total electrolysis charge passed between 0.3 and 0.4 V correlates with a rise in the CO₂ yield over this range.

Table 1 also shows the average quantity of formaldehyde detected and the average total charge passed from the electrolysis of methanol on polycrystalline platinum. The charge maximizes at 0.5 V and follows the same trend with potential as the average current on the forward and reverse sweeps of the voltammogram. The decline in current between 0.6 and 0.8 V on the voltammogram has been attributed to surface blocking by inhibiting oxides,^{4c,12} so it is likely that the charge reduction between 0.5 and 0.6 V is due to this effect. The formaldehyde production follows the same trend as the charge, maximizing at about 0.5 V. It is notable that although formaldehyde accounts for only a small percentage of the total charged passed at potentials more positive than 0.3 V, it is still produced in significant, readily detectable quantities.

The open circles in Figure 3 show results of blank experiments performed by electrolyzing 60 μ L samples of 0.1 M HClO₄. Formaldehyde values from the blanks ranged from 18 to 33 pmol. These experiments demonstrate the formaldehyde formation is tied to the presence of methanol in the reaction solution. Furthermore, the assay of samples containing 15 mM methanol in 0.1 M HClO₄ before electrolysis gave background formaldehyde at the same levels as the blanks.

The appearance of formaldehyde in aqueous methanol solutions following short electrolysis periods provides insights into the pathways and energetics of methanol oxidation on platinum. First, since methanol oxidation to CO₂ releases 6 mol of electrons per mol of methanol, conversion to formaldehyde, a two-electron process, leaves $2/3$ of the oxidizing equivalents unharnessed. This effect on the energy conversion efficiency appears to be important at double layer potentials below about 0.4 V. Second, although formaldehyde itself can oxidize on platinum, converting to CO₂, formate, and adsorbed intermediates, it appears that at low potentials the rate of formaldehyde formation from methanol is much faster than the rate of its oxidation. This behavior has been observed in other studies.^{11a,b,e} The groups of Ota and co-workers,^{11a} Iwasita and Vielstich,^{11b}

and Shibata and Motoo^{11c} observed large quantities of formaldehyde in methanol solutions in contact with platinum at low potentials. Further, Shibata and Motoo observed that modification of platinum with partial coverages of ruthenium or tin decreased formaldehyde yields during methanol oxidation but correspondingly increased the formic acid, demonstrating the possibility that methanol oxidation can progress to formic acid through formaldehyde or a formaldehyde-like intermediate.^{11c} The formaldehyde and formic acid accumulations indicate that methanol oxidation on platinum does not proceed exclusively through C—H bond cleavage to adsorbed CO and provides some support for the possibility that methanol may be converted to CO₂ through pathways that do not involve adsorbed CO.^{1ac-4} Finally, it should be noted that formaldehyde can also affect surface poisoning. The tendency of formaldehyde to form dimers and trimers in aqueous solution^{17,21} can lead to oxidation-resistant surface poisons through adsorption of these multicarbon species on the electrode. Spectroscopic studies indicate that methanolic CO coverages on electrodes are low^{3,8b} and that in addition to adsorbed CO other species, not easily detected by in situ spectroscopic techniques, play a role in surface passivation.^{1ac,3,9,10} It is notable that strong bands due to such carbonaceous species formed from methanol oxidation on platinum-coated gold electrodes have been observed in surface-enhanced Raman spectra.²⁷

In summary, formaldehyde can be generated from methanol oxidation at low potentials on platinum and should be considered as a candidate intermediate in mechanistic work. Further, the insensitivity of modern in situ analysis techniques to formaldehyde should be recognized and more specific assays used in cases where formaldehyde formation is under study.

Acknowledgment. Support of this work by the Office of Naval Research is gratefully acknowledged.

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Formaldehyde Yields from Methanol Electrochemical Oxidation on Carbon-Supported Platinum Catalysts

Christina L. Childers, Huiliang Huang, and Carol Korzeniewski*

Department of Chemistry & Biochemistry, Texas Tech University, Lubbock, Texas 79409-1061

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The formation of formaldehyde during methanol electrochemical oxidation on supported Pt and Pt-Ru catalysts was investigated. While on solid platinum electrodes, the formaldehyde yields from methanol oxidation are near 30% at low potentials; the yields fall below 2% for methanol electrochemical oxidation on carbon-supported catalysts in Nafion. The lower formaldehyde yields, which result from more complete methanol oxidation, are believed to arise from the ability of partial oxidation products to be transported to an array of active catalyst sites dispersed within the three-dimensional network of the Nafion film.

Introduction

The electrochemical oxidation of small, oxygenated organic molecules on platinum and related electrode materials has been widely studied, mainly with fuel cell applications in mind.¹⁻³ These reactions are complicated, as several elementary steps are possible en route to carbon dioxide, and the involvement of the electrode surface gives rise to electronic and geometric effects that are poorly understood and difficult to probe. Furthermore, in reactions among surface species, such as in the formation of carbon dioxide from adsorbed CO and surface oxides, the spatial arrangement of adsorbates can have a strong influence on the reaction rate.

Methanol has served as a model in the study of organic electrochemical oxidation mechanisms, due to its relative simplicity and potential for use in direct methanol fuel cells.¹⁻⁴ The surface chemistry of methanol is rich. Therefore, a great deal of effort has been devoted to identifying adsorbed partial oxidation products and investigating the effects of electrode surface structure and composition on reaction pathways.^{1,5-7} Adsorbed CO formation from methanol has been studied in some detail (cf. refs 8-10). CO can be detected on electrodes down to a few percent of a monolayer with infrared spectroscopy, and the positions and intensities of the vibrational bands provide information about the adlayer structure and the interfacial environment. Adsorbed COH and CHO species have also received attention.^{1,2,7} Although these fragments have been difficult to detect, they are eminently important,

since the optimization of pathways to CO₂ through these non-CO intermediates can improve the energy conversion efficiency.

Soluble species can also form during methanol oxidation.^{11,12} We have been interested in formaldehyde.¹³ As a species formed in the first two-electron oxidation step ($\text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{O} + 2\text{H}^+ + 2\text{e}^-$), formaldehyde accumulation can leave two-thirds of the reaction's oxidizing equivalents untapped. Formaldehyde has been detected during methanol oxidation on Pt electrodes.¹¹⁻¹³ We recently investigated its formation at potentials in the range 0.2-0.6 V (versus KCl-saturated Ag/AgCl).¹³ The rate of formaldehyde formation increased with potential up to 0.5 V. However, the amount of formaldehyde produced relative to the total charge passed (the formaldehyde yield) was greatest at low potentials. The declining formaldehyde yields toward more positive potentials appeared to be offset by increased CO₂ formation.

The present study reports formaldehyde yields for methanol electrochemical oxidation on carbon-supported Pt and Pt-Ru catalysts dispersed in Nafion. These materials are of interest for their potential use in direct methanol fuel cell anodes (cf. refs 4-6 and 14-18). The formaldehyde produced from reactions on carbon supported catalysts, blank carbon-support material, and solid polycrystalline platinum was determined as a function of potential and methanol concentration. Solid polycrystalline platinum gave substantially higher formaldehyde yields than the supported catalysts. The differences are discussed in terms of the catalyst film structure.

* Corresponding author. Phone: 806/742-3059. Fax: 806/742-1289. E-mail: korzeniewski@ttu.edu.

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Experimental Section

Reagents. Pt 10% on Vulcan XC-72R carbon and Pt 30%, Ru 15% on Vulcan XC-72R carbon were obtained from Alfa Aesar/Johnson Matthey Co. (Ward Hill, MA). Vulcan XC-72R carbon was obtained from Cabot (Boston, MA). Solutions were prepared from 18 M Ω water from a four-cartridge Nanopure system (Barnstead, Des Moines, IA). Methanol (Burdick & Jackson, GC grade) was washed over alumina, filtered, distilled, and stored refrigerated. Aqueous solutions containing methanol were prepared fresh the day of each experiment. Perchloric acid (99.999%), Nafion (5 wt % in water and lower alcohols) and 1,3-cyclohexanedione were obtained from Aldrich. 1,3-Cyclohexanedione was purified by vacuum sublimation before use. Ammonium acetate (Aldrich) and hydrochloric acid (Baker) were reagent grade or better and used as received.

Electrochemistry. A KCl-saturated silver-silver chloride (Ag/AgCl) electrode was employed as the reference in all electrochemical experiments. The electrode contacted the electrolyte solution through a Vycor glass frit. The compartment that held the reference was separated from the test solution by a ground glass stopcock to further minimize contamination of the test solution by leakage of chloride. We have been able to use ion chromatography to ensure the chloride levels stay negligible in these small volume electrolysis experiments (see ref 19).

Catalyst materials were prepared for electrochemistry following the procedure of Gamez et al.¹⁵ The powders (50 mg) were mixed as a slurry with 0.5 mL of Nafion solution (5 wt %) in 3.0 mL of deionized water and sonicated for approximately 2 min. Twenty microliters of the suspension was pipetted onto a polished glassy carbon disk electrode (5 mm diameter) and allowed to dry overnight. Before sample electrolysis, an adsorbed catalyst film was cycled between -0.25 and $+1.3$ V (versus Ag/AgCl) in 0.1 M HClO₄ until strong waves characteristic of platinum appeared. Electrolysis was performed on 80 μ L samples of methanol solution with the cell described previously.¹³ Reaction times of 6 and 2 min were employed with 15 mM and 0.3 M methanol solutions, respectively. Immediately after electrolysis, 70 μ L was removed from the cell and diluted with deionized water to bring the formaldehyde concentrations into the range 2–10 μ M.

Formaldehyde Determination. Formaldehyde was determined fluorimetrically following reaction with 1,3-cyclohexanedione using a flow injection arrangement designed around that reported in ref 20. The reagent solution was prepared by mixing 25 mg of 1,3-cyclohexanedione, 16.5 g of ammonium acetate, and 6.5 mL of concentrated HCl in 200 mL of deionized water and then diluting to 250 mL. After injection, the sample (50 μ L) and reagent were incubated 3 min at 95 $^{\circ}$ C and then transported to the flow-through fluorimeter. The sample was excited by a UV lamp (BF350-UV1, JKL Components, Pacoima, CA) with maximum intensity at 365 nm. The fluorescence emission was collected at 460 nm through a 30 nm band-pass filter on the photodetector (Intor, Socorro, NM). The calibration plot in Figure 1 demonstrates the assay sensitivity and precision. The limit of detection is about 60 nM, which is an order of magnitude more sensitive than the lowest formaldehyde levels measured in the methanol oxidation experiments.

Results

Figure 2 shows cyclic voltammograms of catalyst materials in Nafion supported on glassy carbon. The voltammogram for blank Vulcan XC-72R carbon at the bottom of the figure is featureless, and the current is small relative to those for the carbon films that contain metals. The center voltammogram has waves characteristic of Pt. The response compares well with that of similarly prepared films.¹⁵ The oxide stripping peak on the negative-going sweep near 0.2 V and the hydrogen adsorption region between 0 and -0.2 V indicate the presence of Pt in the layer. The top voltammogram shows the response of films containing Pt and Ru. The current in the hydrogen region

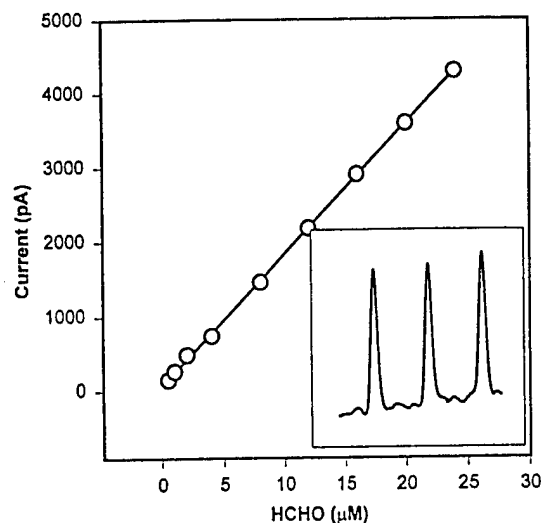


Figure 1. Plot of fluorescence signal versus formaldehyde concentration. The inset shows the response for repetitive sample injections. The equation of the calibration line is $Y = 175.7[\text{CH}_2\text{O}] + 78.3$ ($R^2 = 0.9997$). The assay limit of detection was 62 nM.

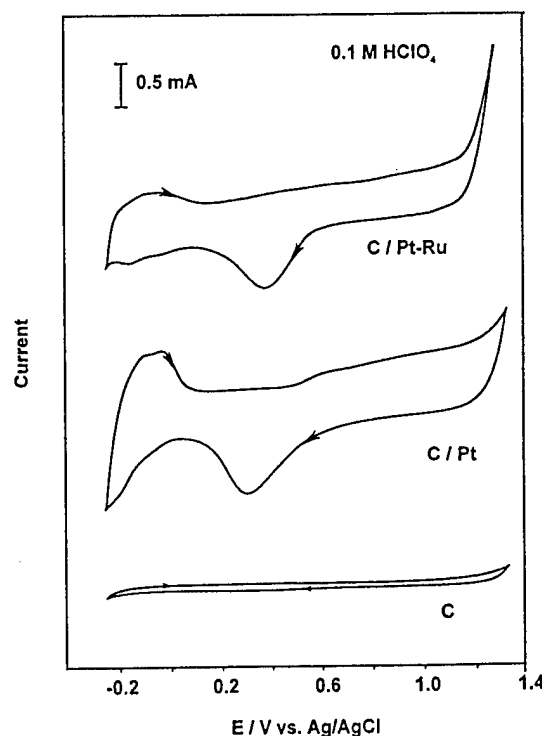


Figure 2. Cyclic voltammograms of catalyst materials in Nafion supported on a glassy carbon electrode. Voltammograms were recorded in 0.1 M HClO₄ at a scan rate of 50 mV/s. Traces are for Vulcan XC-72R carbon (bottom); Pt 10% on Vulcan XC-72R carbon (middle); and Pt 30%, Ru 15% on Vulcan XC-72R carbon (top).

for the Pt–Ru film is diminished compared to that for the film with Pt catalyst. This response is consistent with the behavior of solid Pt–Ru alloy electrodes observed previously.²¹

Table 1 reports the reaction charge and quantity of formaldehyde produced during short periods of methanol

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Table 1. Summary of Charge and Formaldehyde Yields from Methanol Oxidation on the Indicated Electrode Materials

electrode ^a	potential ^b	[CH ₃ OH] ^c	charge ^d (mC)	H ₂ CO ^d (pmol)	H ₂ CO yield ^e (%)
C	0.3	15 mM	1.40	330	4.6
	0.5	15 mM	0.55	230	8.0 ± 0.2
C/Pt	0.3	15 mM	14.55	369	0.5 ± 0.3
	0.5	15 mM	60.5	380	0.1 ± 0.02
	0.3	0.3 M	30.4	2017	1.3
	0.5	0.3 M	42.5	2290	1.1 ± 0.3
C/Pt-Ru	0.3	15 mM	26.5	1651	1.1 ± 0.7
	0.5	15 mM	93.0	1549	0.3 ± 0.06
	0.3	0.3 M	14.1	601	0.8
	0.5	0.3 M	35.6	1165	0.6 ± 0.3
Pt solid	0.3/	15 mM	0.4	565	29 ± 3
	0.5/	15 mM	13.3	3299	5 ± 1
	0.3	0.3 M	0.08	146	36.0 ± 1.7
	0.5	0.3 M	3.6	3209	16.8 ± 2.4

^a The following materials were in Nafion supported on glassy carbon: C = Vulcan XC-72R carbon; C/Pt = Pt 10% on Vulcan XC-72R carbon; C/Pt-Ru = Pt 30%, Ru 15% on Vulcan XC-72R carbon. Pt solid = a solid polycrystalline Pt electrode. ^b Potential versus a KCl-saturated Ag/AgCl reference electrode. ^c The electrolysis times of 6 min for 15 mM and 2 min for 0.3 M methanol were used. ^d The values reported for charge and amount of CH₂O are averages from several experiments. These quantities tended to vary from experiment to experiment; however, the ratio of these quantities (pmols of CH₂O formed to mC charge passed) showed good precision. This precision is reflected in the uncertainties for the % CH₂O yield values. ^e Error bars represent the 95.5% confidence limit determined from two times the sample standard deviation. The yield is computed from the ratio of charge required to produce H₂CO to the total charge passed during the electrolysis period. An H₂CO yield was computed for each experiment, and these values were averaged to give the percentages and uncertainties shown. / From ref 13. See ref 22.

oxidation on the materials studied. It is not appropriate to compare the reaction charge and total moles of formaldehyde detected in experiments with 15 mM and 0.3 M methanol, since the reaction times were different for these two solutions. The higher oxidation current and faster rate of formaldehyde production in 0.3 M methanol made it necessary to reduce the reaction time in this solution. Comparisons can be made among the formaldehyde yields, however. Taking the ratio of the charge required to produce the quantity of formaldehyde detected to the total reaction charge compensates for differences in the reaction times for the two concentrations. Figure 3 summarizes the formaldehyde yields graphically.

In Table 1, the bottom entries for solid Pt indicate formaldehyde formation accounts for about 30% of the total electrolysis charge for reactions at 0.3 V.²² The formaldehyde yields on the solid Pt electrode appear to decrease toward more positive potentials, particularly for the 15 mM methanol solution. This is consistent with previous studies,^{7,9,23} which have shown CO₂ formation becomes dominant at potentials greater than 0.3 V. The topmost entry in Table 1 indicates methanol oxidation occurs to some extent on bare Vulcan carbon immobilized in Nafion, producing moderate amounts of formaldehyde in 15 mM solutions. At 0.3 V, the higher reaction charge for Vulcan carbon compared to solid platinum probably reflects both the higher surface area of the carbon and

(22) The formaldehyde assay used in the present study was slightly different than the assay based on 2,4-pentanedione employed in ref 13. The newer assay allowed a narrow band phosphor-coated UV lamp emitting at 365 nm to be used as the excitation source in a filter fluorimeter dedicated to these measurements. The change of assay did not affect the formaldehyde yields.

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Yields of Formaldehyde from Methanol Electrochemical Oxidation

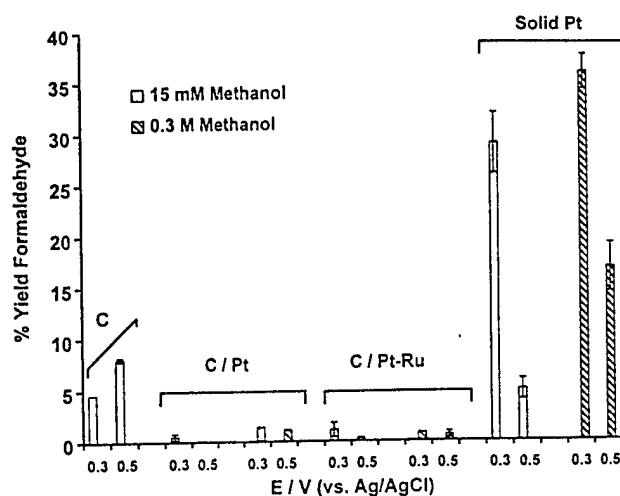


Figure 3. Summary of formaldehyde yields from methanol electrochemical oxidation. Potentials are with respect to a KCl-saturated Ag/AgCl reference electrode. C = Vulcan XC-72R carbon; C/Pt = Pt 10% on Vulcan XC-72R carbon; C/Pt-Ru = Pt 30%, Ru 15% on Vulcan XC-72R carbon. Solid Pt = a solid polycrystalline Pt electrode.

strong poisoning of the platinum at this potential. Entries for C/Pt and C/Pt-Ru in Table 1 show that addition of metal catalyst to the carbon support leads to large increases in the reaction charge and decreases in the formaldehyde yields. Further, the formaldehyde yields remain low for reactions in 0.3 M methanol solutions. These trends are seen more readily in Figure 3. The results indicate the Pt and Pt-Ru deposits are effective catalysts for the electrochemical oxidation of bulk methanol and methanol reaction intermediates generated on the carbon support. It is worth noting that the oxidation of 15 mM methanol on blank Vulcan carbon was examined ahead of that on the supported metal catalysts to identify any background formaldehyde formed by reaction on the support material. After it was determined that the formaldehyde yields on the metal catalysts were below 2% for all methanol concentrations and electrolysis potentials examined, background studies with blank Vulcan carbon were no longer necessary and so were discontinued.

The formaldehyde yields for reactions on the supported catalysts were low at the potentials and methanol concentrations studied and did not appear to be sensitive to metal loading or Ru content. In contrast, formaldehyde yields from methanol oxidation on solid Pt were somewhat higher in 0.3 M solutions than 15 mM solutions. Increased yields of partial oxidation products are expected at higher methanol concentrations, in part, because the decrease in interfacial water activity lowers the rate of surface oxide formation ($\text{H}_2\text{O} \rightarrow \text{OH}_{\text{ads}} + \text{H}^+ + \text{e}^-$).²⁴⁻²⁶ Below 0.3 M, the supported catalysts appear to be much less sensitive to methanol concentration than the solid platinum surface. This response is consistent with the very low quantities of partial oxidation products that have been observed at these methanol concentrations in fuel cells.^{25,26}

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Discussion

The low yields of formaldehyde observed for methanol electrochemical oxidation on carbon-supported Pt and Pt-Ru in Nafion can possibly be attributed to the reaction environment within the Nafion film consisting of a three-dimensional network of catalyst particles. The ability of soluble partial oxidation products to undergo multiple encounters with the array of catalyst sites in the film increases the chances for reactions to progress to completion. We also considered that the low yields may be due to formaldehyde entrapment within the Nafion or adsorption to the carbon support. However, the higher yields for reactions on blank Vulcan carbon make it unlikely that formaldehyde levels in solution are significantly lowered by physical interactions with the film.

The catalyst crystallite structure can also influence the distribution of products; however, this effect should be investigated with the metal crystallites bound to a surface rather than immobilized within a permeable film, so the multiple site interactions discussed above can be minimized. Experiments with single-crystal materials have shown the products in organic oxidation reactions are sensitive to the atomic level structure of the electrode surface.^{10,19,27-29} Dissociative chemisorption rates tend to be faster on high-step-density Pt surfaces compared to

smooth Pt(111). However, at low potentials stepped surfaces can be more susceptible to poisoning,^{10,19,27} presumably because of the high adsorbed CO coverages possible at the steps.^{10,19,27,30} The use of techniques to deposit metal catalyst particles on solid carbon supports will allow better studies of catalyst structural effects on organic oxidation pathways.

The different formaldehyde yields on solid Pt electrodes and metal nanocrystals dispersed in Nafion raise questions about relationships between results of electrochemical experiments with solid metal electrodes and the processes these studies aim to mimic in fuel cells. It appears that, in addition to effects of surface structure and composition, model studies should also consider how product distributions can be influenced by the arrangement of metal catalyst particles on the micron and nanometer scales.

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